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TECHNICAL REPORT

67-52--CM

PREPARATION AND CHARACTERISTICS OF CALCIUM SALT  
OF NYLON-ACRYLIC ACID GRAFT POLYMER

by

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## FOREWORD

In recent years, various methods have been developed for the graft copolymerizing of monomers on existing polymer chains. The resulting products frequently display chemical properties introduced by the grafted portion of the molecular structure while retaining the major physical characteristics of the polymer backbone.

Such graft copolymers offer considerable promise in the field of textile fibers. In particular, the calcium salt of the copolymer of acrylic acid and nylon 6,6 has been found to offer a high degree of thermal protection in military uniforms.

The present report covers a study of some of the parameters which determine the rate and level of uptake and removal of calcium ion, as well as initial studies of the dyeing of acrylic-nylon graft copolymers.

The work described here was carried out in the Textile Dyeing Division of the Clothing and Organic Materials Laboratory, under the Textile Materials Project 1C024401-A39, during the period from July 1964 to February 1966.

This program was carried out under the direction of Frank J. Rizzo, Chief of the Textile Dyeing Division.

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## ABSTRACT

The calcium salt form of nylon 6,6 fiber graft-polymerized with acrylic acid has been reported to show considerable promise in the preparation of flash-resistant fabrics. This report covers the initial phases of a systematic study of the significant parameters involved in the preparation of the calcium form from the acid form, and the characteristics of the calcium form under various treatments in water solution.

The rate of sorption of calcium ion from calcium acetate solution was affected primarily by changes in temperature - the desired value of 3.5 percent calcium being attained in approximately 5 minutes at 100°C, 9 minutes at 70°C, and 64 minutes at 30°C. A continuous process for treatment at the highest temperature may, therefore, be possible.

The effect of solution concentration on rate of calcium sorption was much less significant, and increases in solution concentration above 1 percent caused no change in rate.

The amount of calcium sorbed at equilibrium was slightly higher at 70°C (3.90%) than at 100°C (3.80%), as would be expected for an exothermic process. Unexpectedly, however, the amount taken up at 30°C was lower (3.55%) than either of these, suggesting a change in the character of the fiber at the lowest temperature.

The relationship of equilibrium calcium sorption to solution concentration was found to follow the form of the Langmuir isotherm, at both 30° and 100°C. This might be expected for a chemisorption process, such as is probably involved here.

The removal or desorption of calcium from the previously-reacted fiber was difficult with neutral detergents or soaps, but was readily accomplished with a calcium-complexing phosphate or by an acid.

The effect on calcium content of dyeing of the fiber appears thus far to be primarily the effect of the acidity of the dyebaths used, rather than competition between calcium and dye for the available dye sites.

PREPARATION AND CHARACTERISTICS OF CALCIUM SALT  
OF NYLON-ACRYLIC ACID GRAFT POLYMER

1. INTRODUCTION

In work carried out at the U. S. Army Natick Laboratories on the resistance of fabrics to thermal radiation<sup>(11)</sup>, a graft copolymer of acrylic acid on a nylon 6,6 backbone gave very promising results.

The synthesis of this type of polymeric fiber is described in patents<sup>(18,9)</sup> and other literature<sup>(10,8)</sup>. For fibers of the type discussed in this report, nylon 6,6 fiber (polyhexamethylene adipamide) is impregnated with aqueous acrylic acid for sufficient time to permit equilibrium sorption of the acid in the amount of 3 to 22 percent. After being subjected to a total radiation of 1 to 2 Mrads from a source of ionizing radiation (such as an electron beam from a 2-mev Van de Graaff accelerator), the fiber is washed with water to remove the unreacted acrylic acid and ungrafted homopolymer (polyacrylic acid).

According to the literature<sup>(10)</sup>, approximately half of the nylon remains ungrafted in this procedure. Calculations based on the data given suggest that the resulting structure resembles that of the nylon itself but with half of the nylon molecules (120 monomer units long) having one side-chain each, consisting of polyacrylic acid (175 monomer units long). Since the process of preparation involves diffusion of the monomeric acid into previously prepared nylon 6,6 fiber, the polyacrylic acid is probably localized in those regions which were not highly ordered in the original nylon fiber.

Ordinary commercial nylon 6,6 has been found to contain approximately 0.05 milliequivalents per gram of amine groups and 0.09 milliequivalents per gram of carboxylic acid groups<sup>(4,13)</sup>. The data given in the literature<sup>(10)</sup> indicate that the overall composition of the graft copolymer includes approximately 15-20 percent homopolymerized acrylic acid, occurring as side-chains, or about 2.0 milliequivalents per gram of carboxylic acid groups<sup>(7,8,14,18)</sup>.

Treatment of such fibers by suitable reagents shows physical characteristics (sorption, etc.) related to the probable amorphous nature of the polyacrylic acid side-chains, and chemical properties related to the relatively large number of carboxylic acid groups present. These characteristics include increased moisture pickup (compared to nylon 6,6) and the ability to react with metallic ions<sup>(9,10,18)</sup>.

Of the metallic salt derivatives reported, the calcium form has shown the greatest increase in softening point\* over the base nylon<sup>(18)</sup>.

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\*Determined by observing the effect of dropping heated glass beads on the surface of the fabric.

It is this form, also, which has been found to be most promising in resistance to carbon-arc radiation(11).

In the work reported here, we have begun the study of the basic parameters that affect the sorption and desorption of ions such as calcium by a nylon-acrylic acid copolymer. Initial data on the dyeing characteristics of the calcium form are also reported here.

## 2. OBJECTIVE

The objective of this program is to determine the effect of such parameters as time, temperature, and reagent concentration on the sorption and desorption of calcium and similar ions by a graft copolymer of nylon 6,6 and acrylic acid, and to study both the effect of various dyeing procedures on the calcium content of treated fiber and the effect of calcium content on previously dyed fiber.

## 3. WORK DONE AND RESULTS OBTAINED

### a. Discussion of Samples

Except where specifically noted, all of the work described in this study was carried out on copolymer which has been prepared in the acid form then converted to the calcium form to facilitate spinning and weaving. This conversion involved treatment with 2 percent calcium acetate solution for 2 hours at 62-72°C to obtain a calcium content of approximately 3.6 percent in the final, rinsed sample.

The fabric was then subjected to normal preparation for dyeing - scouring in non-ionic detergent solution, and heat-setting to stabilize its structure (50 sec. 205°C).

For our work, this prepared fabric (a 7.5 oz. poplin) was reconverted to the acid (hydrogen) form by treatment with hydrochloric acid, as described in Appendix A.

### b. Rate of Calcium Sorption by Fiber

#### (1) Effect of Temperature on Rate

In the present work, all treatments beyond those described in 3(a), above, were carried out in laboratory equipment, with efficient stirring and temperature control (max.  $\pm 25^{\circ}\text{C}$ ).

In order to facilitate comparison with plant conditions, comparison of the two sets of conditions is given in Table I. (Experimental details are given in Appendix B).



TABLE I  
COMPARISON OF JIG AND LABORATORY CONDITIONS

	<u>Jig (large sample)</u>	<u>Lab (small sample)</u>
Concentration calcium acetate, %	2	2
Calcium Acetate (on wt. of fiber), %	20	30
Liquor-to-fabric ratio	10:1	500:1
Temperature of bath, °C	62-72°	See Data

Samples of fabric (3-5 replicates) were treated in an "infinite bath"\* of 2 percent calcium acetate at 30°, 70°, and 100°C. The calcium content was determined by chelometric titration of the ashed fabric, using disodium ethylenediamine-tetracetic acid and Hydroxynaphthol Blue indicator (Appendix C).

As shown in Figure 1, the fabric took up calcium ion rapidly from the 2 percent solution, reaching an apparent saturation or equilibrium value in about 10 minutes at 100°C. This effect is shown more clearly in Figure 2, where the amount of calcium sorbed is plotted against the square root of time.

In general, the rate curves (Figures 1 and 2) showed a rapid rise at first, then levelled off as the amount of sorbed cation appeared to approach a limiting value. This pattern is characteristic of the sorption of many ionic dyes by nylon or wool, where the dye anions presumably bond to cationic sites on the fiber molecules(1,2,4,5,23, et al).

If diffusion through the polymer fiber is the rate-controlling step in the overall process of sorption of calcium ion, we may compare our data with results predicted for such diffusion. The simplest of these, Fick's Law, is based on the simple relationship<sup>(20)</sup>:

$$\left( \frac{dm}{dt} \right) = D \left( \frac{dc}{dx} \right)$$

Where m = amount sorbed  
t = time  
c = concentration  
D = constant  
x = distance in direction of flow

\*Volume of bath used was sufficient to keep the change in calcium acetate concentration to less than 1 percent of the amount present during the treatment being studied.

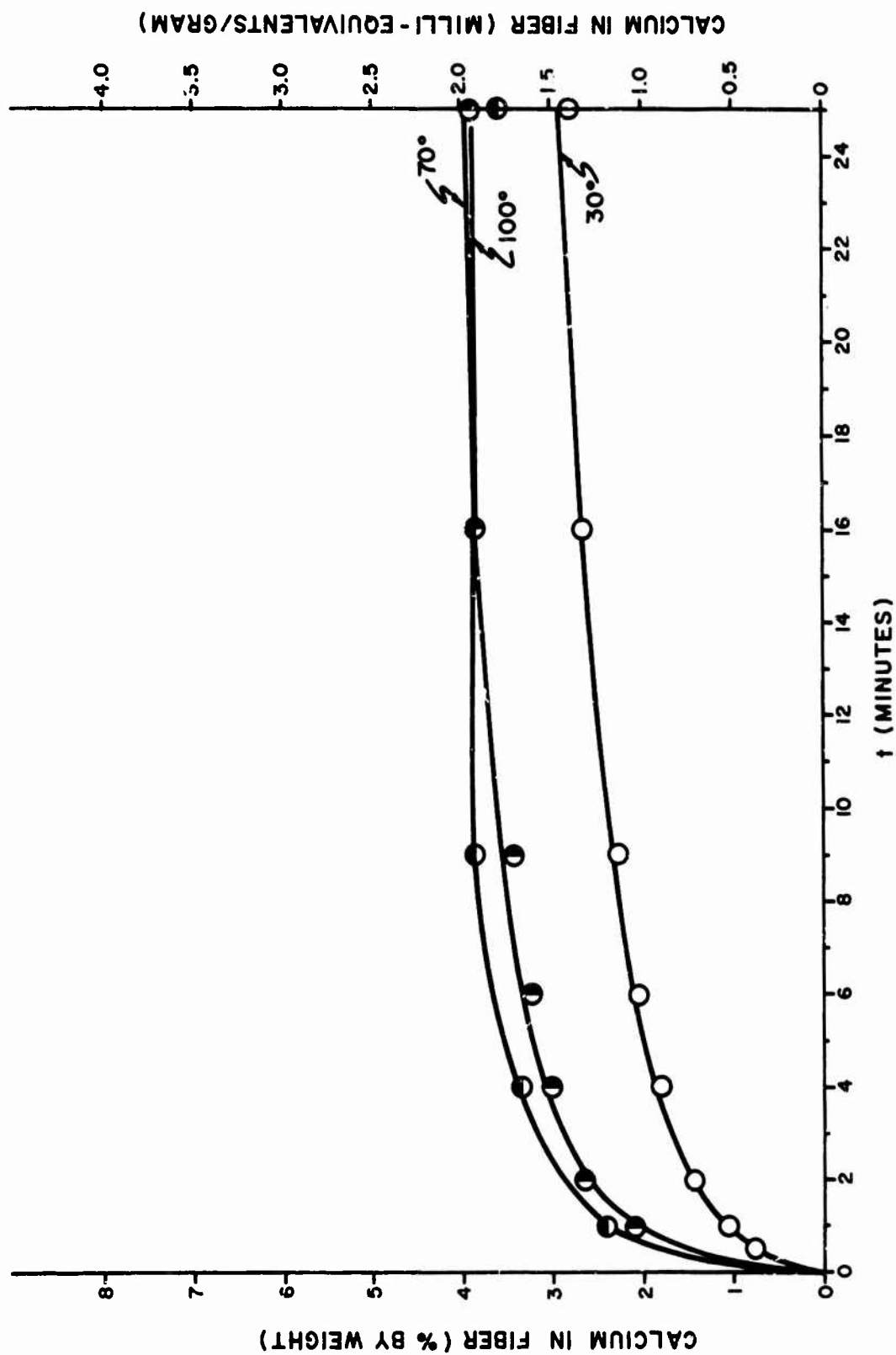


Figure 1. Effect of Temperature on Calcium Sorption From 2% Calcium Acetate Solution (Linear Plot)

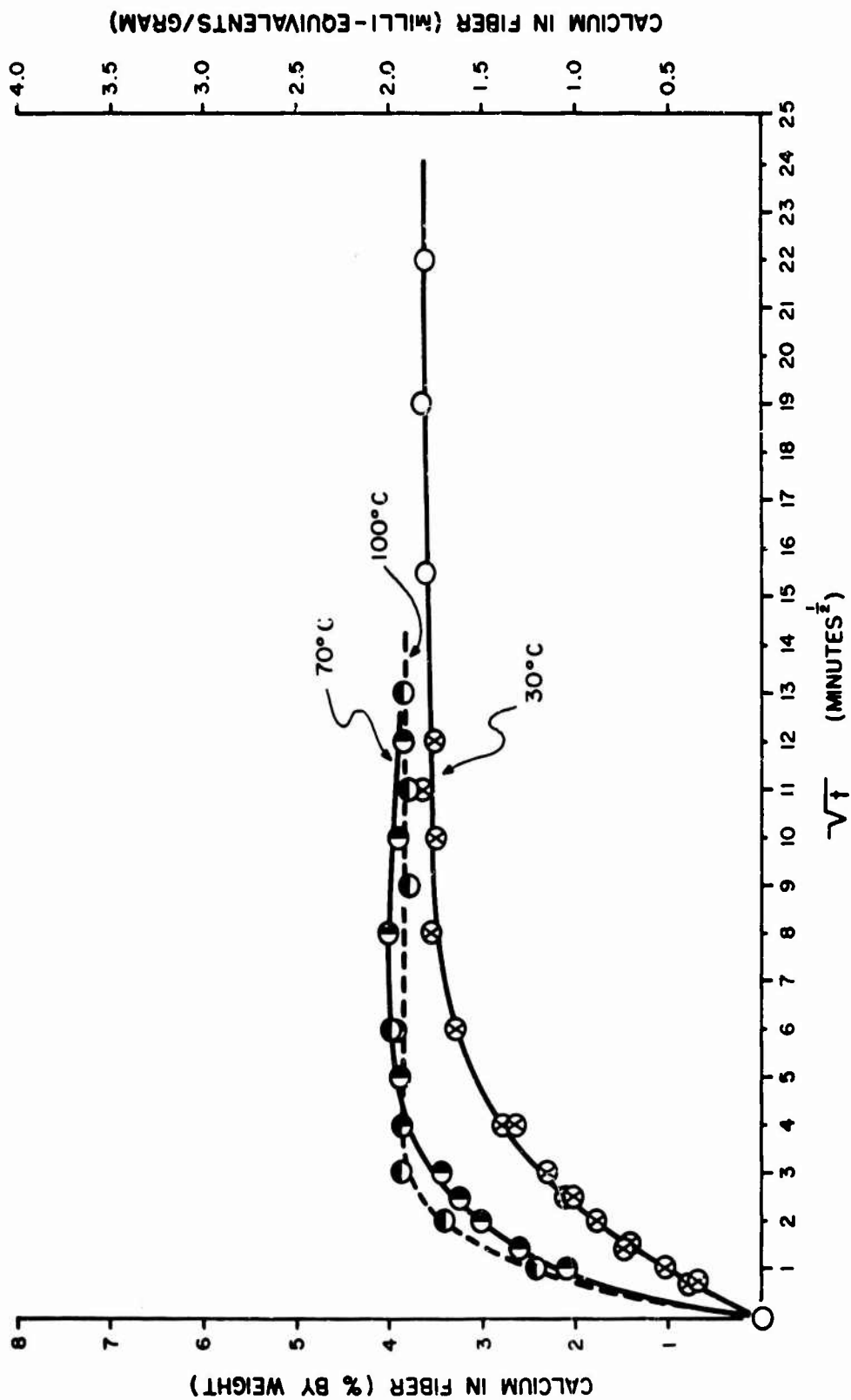


Figure 2. Effect of Temperature on Calcium sorption from 2% Calcium Acetate Solution (Square Root Plot)

This expression, which relates the rate of transfer to the concentration gradient by means of a diffusion constant, leads to a linear relationship between the amount of diffusing substance and the square root of time.<sup>(7)</sup> The expression describes diffusion into films, but diffusion into fibers sometimes shows the linear relationship just described, in its initial stages.<sup>(22)</sup>

In the present work, the rate of calcium uptake shows a linear relationship to the square root of time for a short period at low temperatures and solution concentrations (Figure 3). A comparison of these and later data with more complex expressions for diffusion into fibers will be attempted in future work.

From the more practical viewpoint, it is important to note that the lowest temperature studied (30°C), the rate of calcium sorption was substantially lower than at 70° and 100°C. However, the difference in rate of uptake between 70° and 100° was small (Figure 2).

In each curve (note particularly Figure 2), there is a point in time beyond which the rate of calcium uptake is very low. Carrying the process of sorption past this point would offer little advantage in a practical process. Values of calcium content and time for this point on each curve are listed in Table II in the column headed "Breakpoint." The time required to reach a calcium content of 3.5% is given in the next column. (This value (3.5%) is characteristic of those samples showing promising thermal behavior<sup>(11)</sup>.) The data in this column indicate that the desired value of 3.5% calcium can be obtained in about five minutes at 100°C, - a period short enough to suggest that a continuous process may be feasible.

TABLE II  
RATE OF SORPTION OF CALCIUM ION

Temp. (°C)	Breakpoint		Time to 3.5% Ca (min)	Ca at 2 hrs. (%)
	Time (min)	Ca (%)		
100	10	3.8	5	3.8
70	16	3.8	9	3.9
30	64	3.5	64	3.5

#### (2) Effect of Calcium Concentration on Rate

In order to measure the effect of changes in calcium concentration on the rate of calcium sorption, samples of fabric were treated at 30°

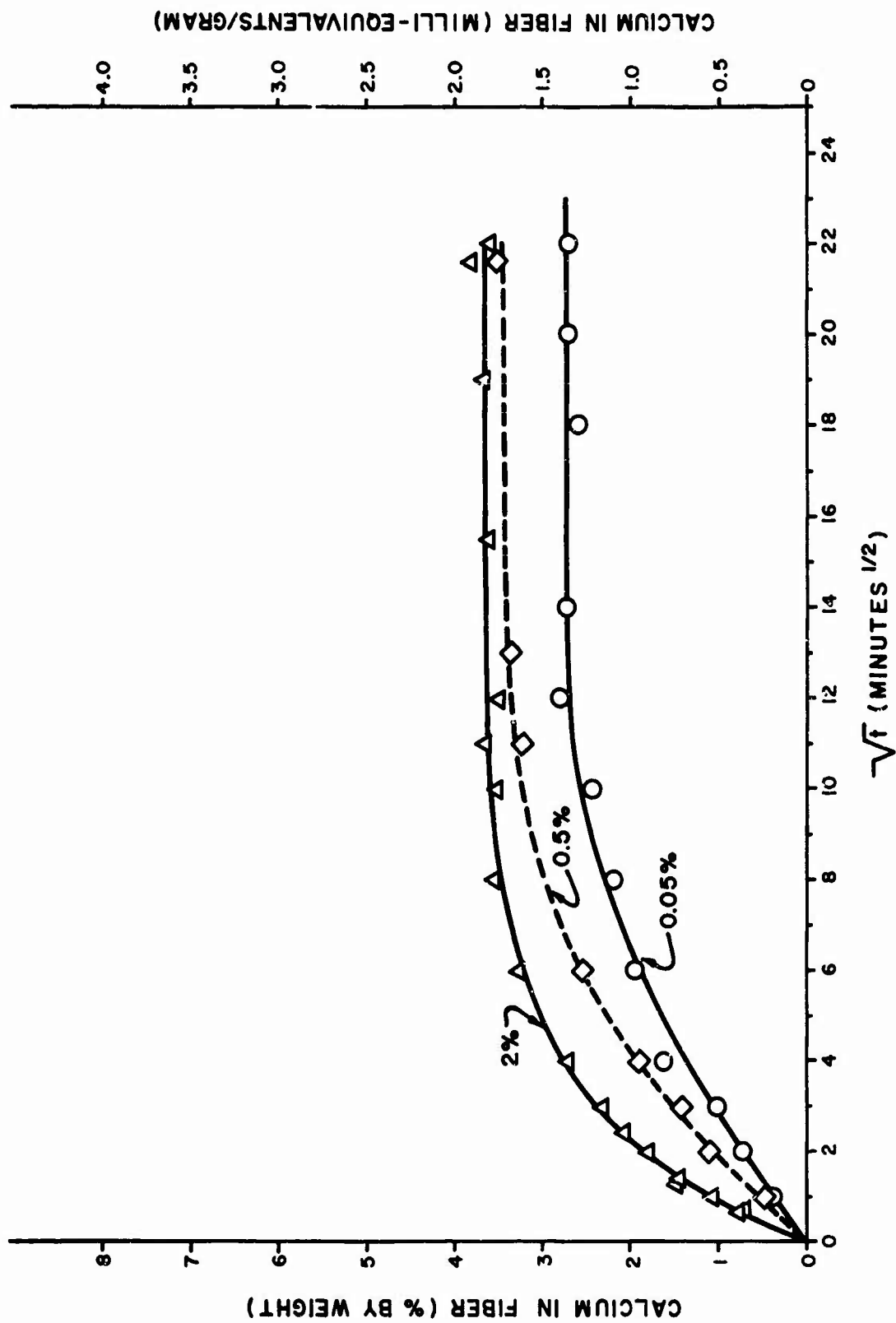


Figure 3. Effect of Concentration on Calcium Sorption From Calcium Acetate Solution at 30°C

and 100°C at five solution concentrations, from 0.05 percent to 2.0 percent calcium acetate. The data are plotted against the square root of time in Figures 3 and 4.

The copolymer being studied here possesses a large number of potentially anionic carboxylic acid groups in the form of polyacrylic acid side-chains. To the extent that such a surface is ionized, it would be expected to have a high zeta potential. Beckmann and Glenz<sup>(5)</sup> have pointed out that when a certain solution concentration is reached, such a fiber should have a surface that is saturated with cations from the surrounding solution. Above such a concentration, the surface layer should remain substantially independent of solution concentration.

This does, indeed, appear to be the case with the copolymer in calcium acetate solution. At 100°C (Figure 4), the rate of sorption from 1 percent solution appears to be identical with that from the 2 percent solution.

From a practical point of view, this means that the rate of calcium uptake from a 2 percent solution will remain unchanged until the bath is over 50 percent exhausted. (It should be pointed out here that the data points on the curves in Figures 1 through 5 are marked by circles having a radius approximately equal to two standard errors of the mean for three readings. This statistic was calculated from a group of 60 determinations, as shown in Appendix D).

#### c. Equilibrium Sorption of Calcium on Fiber

##### (1) Effect of Temperature on Equilibrium

In order to study the effect of temperature on the quantity of calcium sorbed at equilibrium from calcium acetate solution, the process was carried beyond the point where the rate curves appeared to level off (Figure 2).

At 70° and 100°C, the amounts of calcium taken up at apparent equilibrium (Table II) differed by only a small amount - 3.90 percent at the lower temperature; 3.80 percent at the higher temperature. Clearly, in this temperature range, the primary effect of a change in temperature will be a change in rate rather than in equilibrium calcium content.

In general, the reaction of ionic dyes with fibers having suitable dye sites has been found to be exothermic.<sup>(21)</sup> In the present work, therefore, we would expect to find that more calcium is taken up at lower temperatures. In fact, we did find that the amounts taken up at 70° and 100° differed in this manner, as noted above.

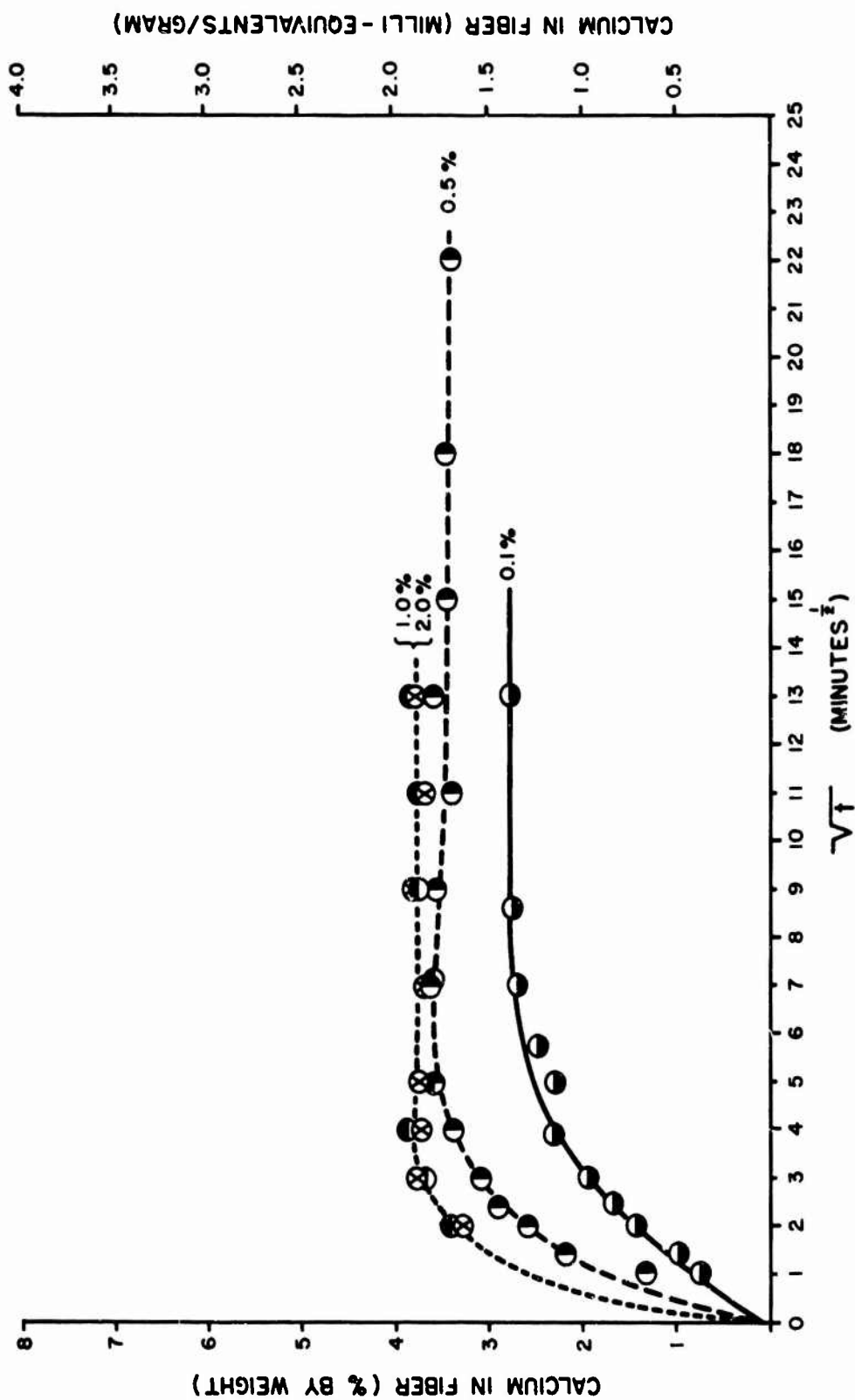


Figure 4. Effect of Concentration on Calcium Sorption From Calcium Acetate Solution at 100°C

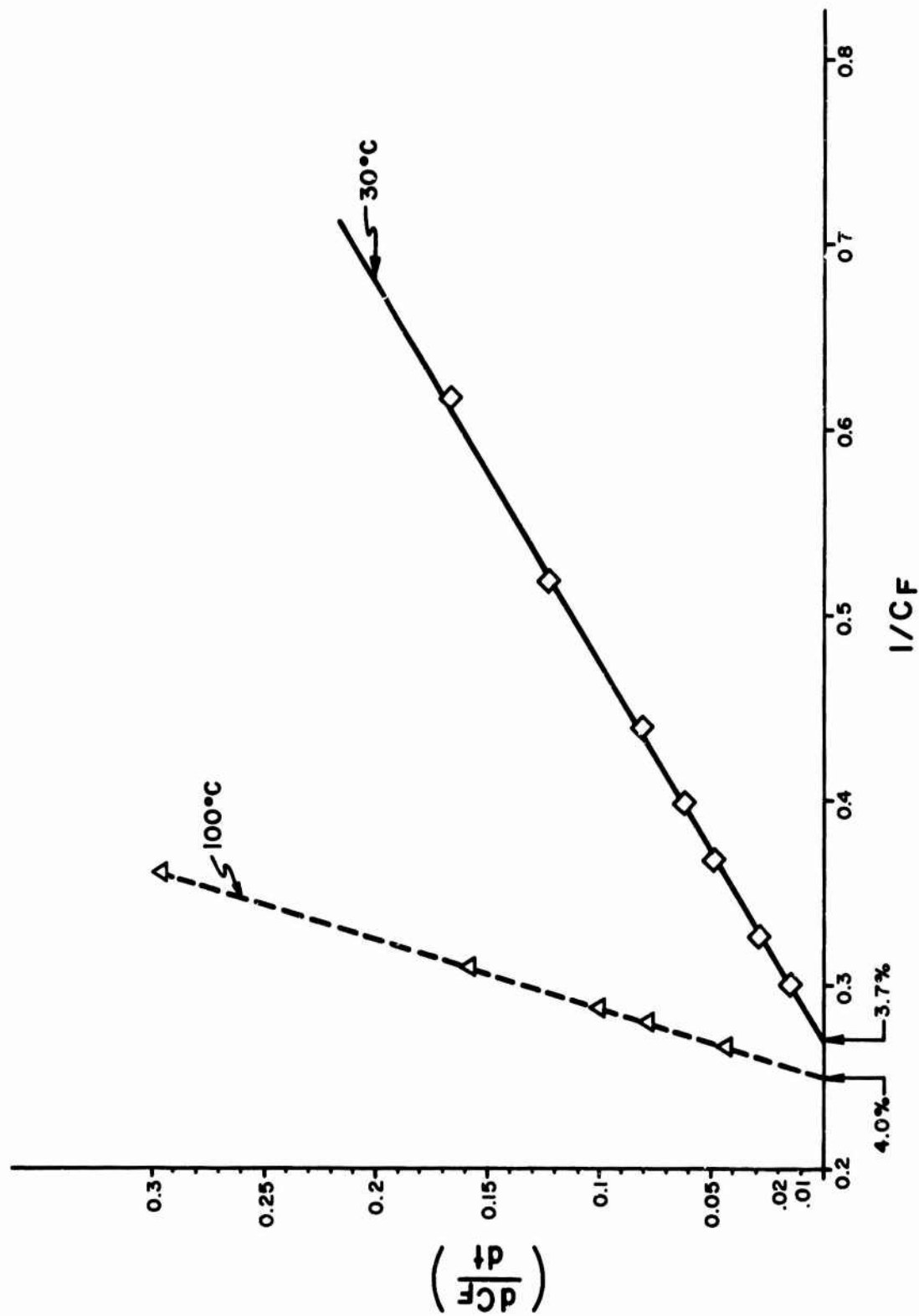


Figure 5. Maximum Calcium Sorption by Extrapolation (2% Calcium Acetate Solution)  $C_F$  = Concentration of Calcium Ion on Fiber:  $t$  = Time in Minutes



However, at 30°C, the value obtained instead of being larger than that for 100°C (3.80%), was somewhat smaller (3.55%). Although the difference is not large, it appears to be real, and consideration was given to possible sources for the deviation from the expected value.

The most obvious explanation would simply be that equilibrium had not been reached at the lowest temperature, since no supporting proof of equilibrium had been obtained. However, when the process was continued for 10 days beyond the point (5 hours) at which equilibrium was apparently reached, no further change in the amount of calcium sorbed was discernible.

Moreover, when the value of the slope of the rate curve (determined by observation) was plotted against the reciprocal of the fiber calcium content<sup>(20)</sup>, a straight line was obtained (Figure 5). Extrapolation led to calcium values that presumably would have been attained had the process been continued in the same manner until a zero slope was reached. Although the extrapolated values differ slightly from those just described, the value at 30°C (3.7%) is again less than 100°C (4.0%).

It appears possible, then, that the sites on the fiber are less accessible at 30°C than at 100°C. The glass transition temperature ( $T_g$ ) which would be related to the accessibility of the polymer structure is not known. The type of polymer used in the backbone (nylon 6,6) is reported to have a  $T_g$  of 50°C<sup>(12)</sup> in the dry state. For a polymer in contact with water,  $T_g$  should be lower.<sup>(17)</sup> From our data, however, we can conclude only that at some temperature less than 70°C, the sites in the copolymer become less accessible.

An alternative explanation for the data may be found in experimental results obtained during the preparation of this report. Rate curves for sorption of calcium from dilute solutions at intermediate temperatures (70°C) show a distinct break after a moderate interval of time (approximately 40 minutes), suggesting a two-stage process similar to that reported for cellulosic polymer and summarized by Rogers.<sup>(15)</sup> In such a system, the first stage may be controlled by diffusion, and the second jointly by diffusion and polymer relaxation.

Should such a system be represented by the data obtained at 30°C in the present work, the levelling-off observed here (Figure 3) may be merely a quasi-equilibrium state preceding a second sorption stage, not reached during the experiment.

## (2) Effect of Calcium Concentration in Solution

In order to determine the effect of concentration of calcium acetate in solution on the equilibrium uptake of calcium ion, sorption

curves were carried to apparent equilibrium at several concentrations, at both 30° and 100°C (Figures 3 and 4).

The Langmuir theory<sup>(6)</sup>, used to describe certain sorption processes, is based on several assumptions, including sorption on specific sites and saturation of each site by a reacting particle. These requirements are met by the present system. On the other hand, it is difficult to see how the acid groups of the homopolymerized side-chains act independently of each other (another postulate of the Langmuir derivation); nevertheless, the equilibrium data obtained fit the Langmuir type of isotherm quite well. The distribution ratio of calcium between fiber and solution varies linearly with solution concentration at both 30° and 100°C as shown in Figure 6.

### (3) Maxima in Sorption Curves

It will be noted in Figures 2, 3 and 4 that some of the sorption rate curves go through a slight maximum. Similar maxima have been pointed out, with no attempt at interpretation, by workers studying the sorption of acids by nylon 6,6<sup>(7,14,19)</sup>. In another instance, maxima in dyeing curves were attributed to contamination.<sup>(3)</sup>

Examples of a similar "overshoot" found in the sorption of water by wool have been attributed<sup>(15)</sup> to a high heat of solution leading to a localized increase in temperature with consequent increase in sorption capacity. Whether the maxima observed in the present work can be related to the process of wetting or swelling the fiber might be studied by comparing the present data with curves for fibers previously soaked to equilibrium in water. Work in this area is planned.

### d. Desorption of Calcium From Fiber

#### (1) Desorption by Surfactants and Complexing Agents

Since the calcium form of the nylon-acrylic acid graft copolymer is potentially the most valuable to the Army from the point of view of flash protection, the ability of the fiber to remain in this form when subjected to various wet treatments is important. The calcium form of the fiber was treated with several solutions representative of those likely to be used in the treatment of finished fabrics. Results are given in Table III. It will be noted that, for most reagents, the data were obtained after one hour at 100°C.

One of the most effective reagents shown in Table III (sodium hexametaphosphate) was then subjected to further study. Initial work on the rate of sorption of this common calcium-complexing agent gave the results plotted in Figure 7. This curve shows a sharp drop in

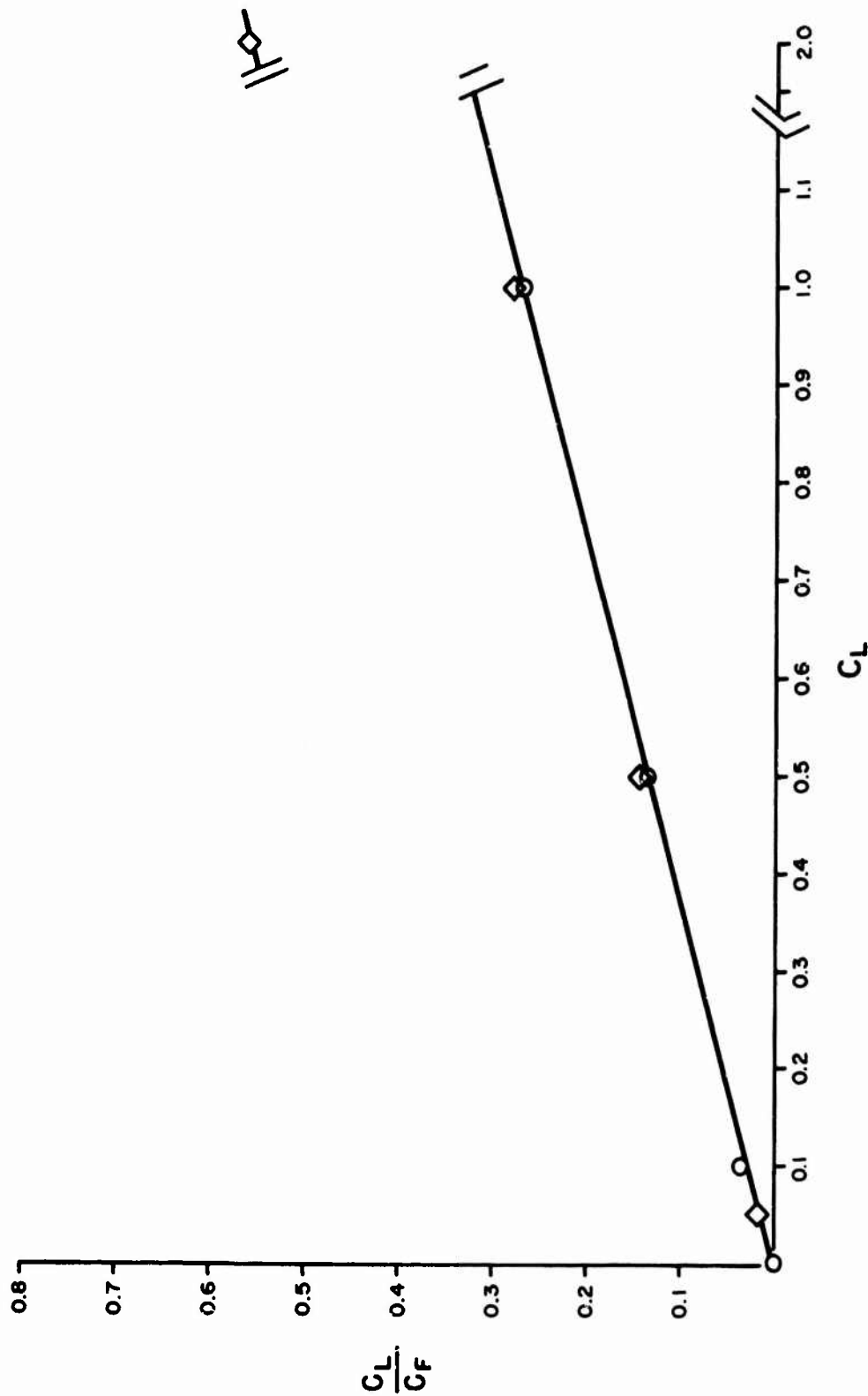


Figure 6. Sorption Isotherms for Calcium From Calcium Acetate Solution ( 30°C, 100°C).  $C_L$  = Concentration of Calcium in Solution.  $C_F$  = Concentration of Calcium Ion in Fiber

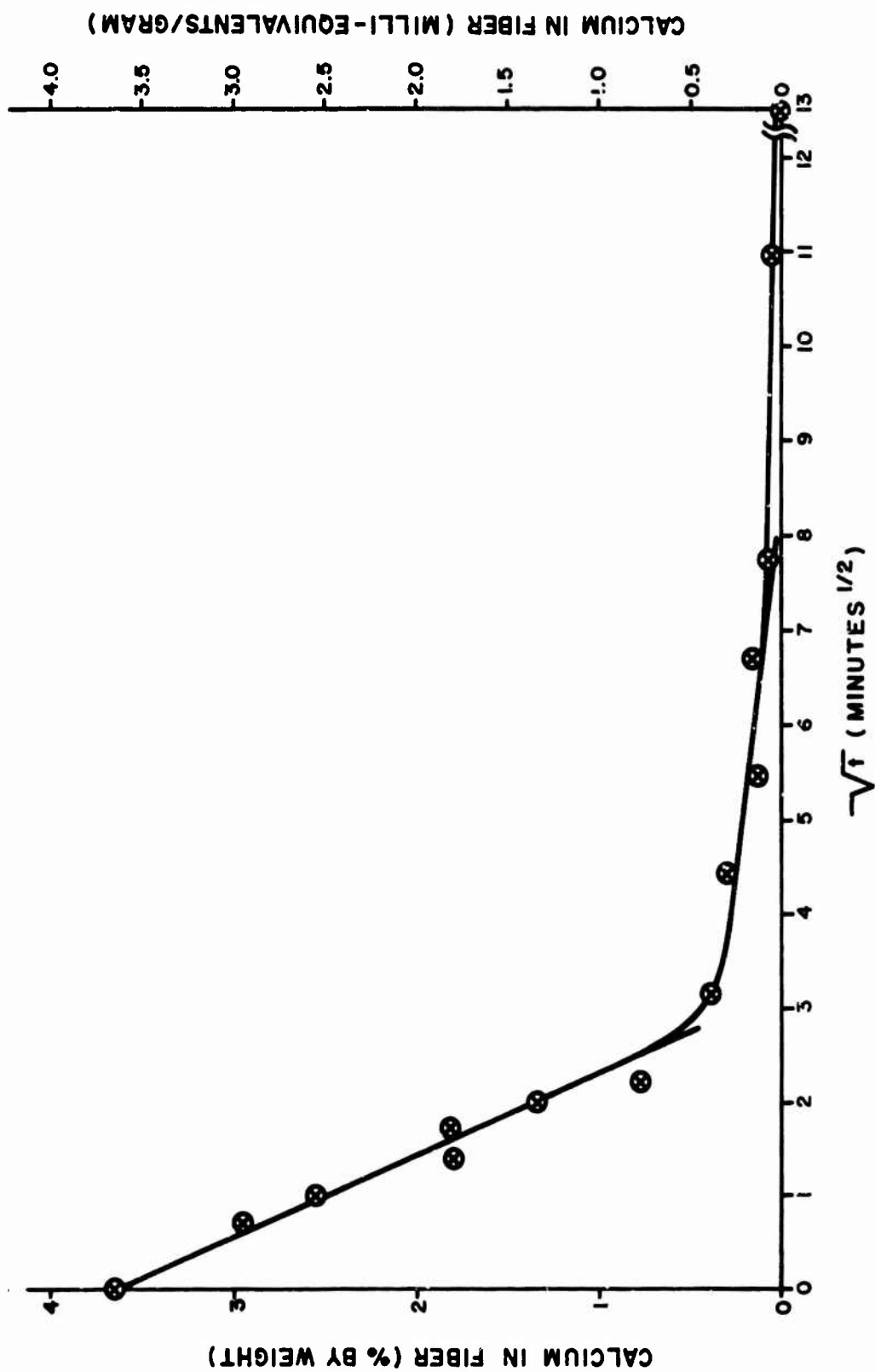


Figure 7. Desorption of Calcium by Sodium Hexametaphosphate (2% Solution, 30° C)

calcium content on exposure to a 2 percent sodium hexametaphosphate solution, even at the moderate temperature of 30°C - approximately 85 percent of the calcium being lost in the first five minutes.

TABLE III  
LOSS OF CALCIUM FROM CALCIUM FORM OF THE FIBER

<u>Reagent</u>	Temp. (°C)	Time (min)	<u>Calcium</u>		Ca Loss (%)
			Before	After	
Sodium hexametaphosphate*, 2%	30	180	3.67	.04	3.63
	100	60	3.67	.70	2.97
Sodium laurylsulfate, 2%	98	60	3.64	3.64	0
Calgon**, 2%	100	60	3.64	1.78	1.86
Tetrasodium pyrophosphate, 1%	100	60	3.64	1.69	1.95
Standard laundering	(see Appendix E)		3.71	3.54	.17
Sodium carbonate, 2%	100	60	3.71	3.48	.23
Sodium chloride, 2%	100	180	3.67	3.29	.38
Water, distilled	100	180	3.67	3.69	0
Fullers soap***	70	20	3.64	3.45	.19

The significance of this set of data in relation to laundering or other wet treatments is apparent. Clearly, the use of phosphates, which are commonly encountered in laundering formulations, is inadvisable if the calcium content of the fiber is to be maintained at nearly maximum level.

## (2) Desorption by Acid

In the course of preliminary experiments in the dyeing of the calcium form of the nylon-acrylic acid graft copolymer (described in the following section), a marked loss of calcium was noted. In accordance with usual practice, the dyeings were carried out in the acid solution, hence

\*Approximate formula:  $\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$  (Technical Grade)

\*\*A commercial mixture of sodium phosphates

\*\*\*Formulation: 5 oz. soap, 3 oz.  $\text{Na}_2\text{CO}_3$ , 0.25 oz. Quadrafos (sodium tetraphosphate)

the loss of calcium could be attributed to replacement of the calcium counter-ion by the proton from the dissolved acid, either because the fiber acid is weaker, or because of a shift in equilibrium.

Treatment of the calcium form of the fiber with either hydrochloric or acetic acid (approximately pH = 2.5) at 100°C for two hours resulted in reduction of the calcium content to very low levels (around 0.04%). Because of the relevance of this to customary dyeing procedures, a more detailed study of the acid desorption process was begun and will be reported later.

#### e. Dyeing of Calcium-Treated Fiber

##### (1) Cationic Dyes

According to dye-site theory(13,16,21), ionic dyes are sorbed by a fiber in stoichiometric amounts proportional to the number of appropriate ionic sites in the fiber structure. On the fiber being studied, the dye sites for cationic dyes would presumably comprise the carboxylic acid groups derived from the grafted acrylic acid, together with the much smaller number of such groups located at the ends of the nylon backbone of the fiber.

From the equilibrium data on calcium sorption (given in this report), the number of available carboxylic acid groups may be calculated. Assuming each calcium ion reacts with two such acid groups, the 3.8 percent calcium generally found would correspond to approximately 1.9 milliequivalents per gram of fiber.

In the case we are considering, the dye ion and the calcium ion, being both cationic, would presumably compete for the same anionic carboxyl sites on the fiber. As a result of this competition, we would expect a cationic dye in solution to displace some or all of the calcium previously applied to anionic fiber substrate. In fact, when an excess of Methylene Blue (a cationic phenothiazine dye) was applied to the calcium form of the acrylic-nylon graft copolymer, only 10 percent of the calcium was lost. Because of the importance of this type of reaction in the present study, more work in this area is planned.

##### (2) Anionic Dyes

For anionic ("acid") dyes, the dye sites on the nylon-acrylic acid graft copolymer would presumably be those same protonated amine groups present on the unmodified polymer (nylon 6,6), since the grafted polyacrylic acid groups would not possess the required positive charge. Such

positively charged sites would be found on the nylon at the terminal amino groups, which presumably would exist in protonated form at the hydrogen-ion concentrations customarily used for acid dyeing, (pH 2.5 - 5.0).

When the fiber in the calcium form was dyed with Acid Green 25 (an anionic dye of the anthraquinone type) at a pH of 4, the calcium content dropped sharply (from 3.6 to .03%). This marked effect is most readily attributed to the acidity of the solution, an effect already discussed above.

The observations and conclusions made in the section referred to would probably apply in general to those anionic dyes that are applied at a low pH. However, certain types of anionic dyes -- neutral-dyeing premetallized dyes; and neutral-dyeing ("milling") acid dyes -- may be applied from near neutral solutions; hence, a study of such dyes is planned.

#### 4. Conclusions and Recommendations

Although the work under the program described in this report is continuing, certain conclusions may be drawn from the results found thus far.

The rate of formation of the calcium salt of the acrylic acid graft copolymer of nylon 6,6 is affected chiefly by temperature. Changes in concentration of the reactive solution have little effect above a certain level.

For the samples studied, essentially the entire amount of calcium reacted at equilibrium is required for desired protection against thermal radiation. Hence, processes for preparation of the calcium derivative should utilize maximum practicable temperatures. Data indicate that a continuous process is possible since calcium is removed from the salt form of the copolymer most readily by complexing agents and by acids.

Treatments (such as laundering) intended to retain the calcium should avoid these reagents.

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## APPENDIX A

### Preparation of Samples

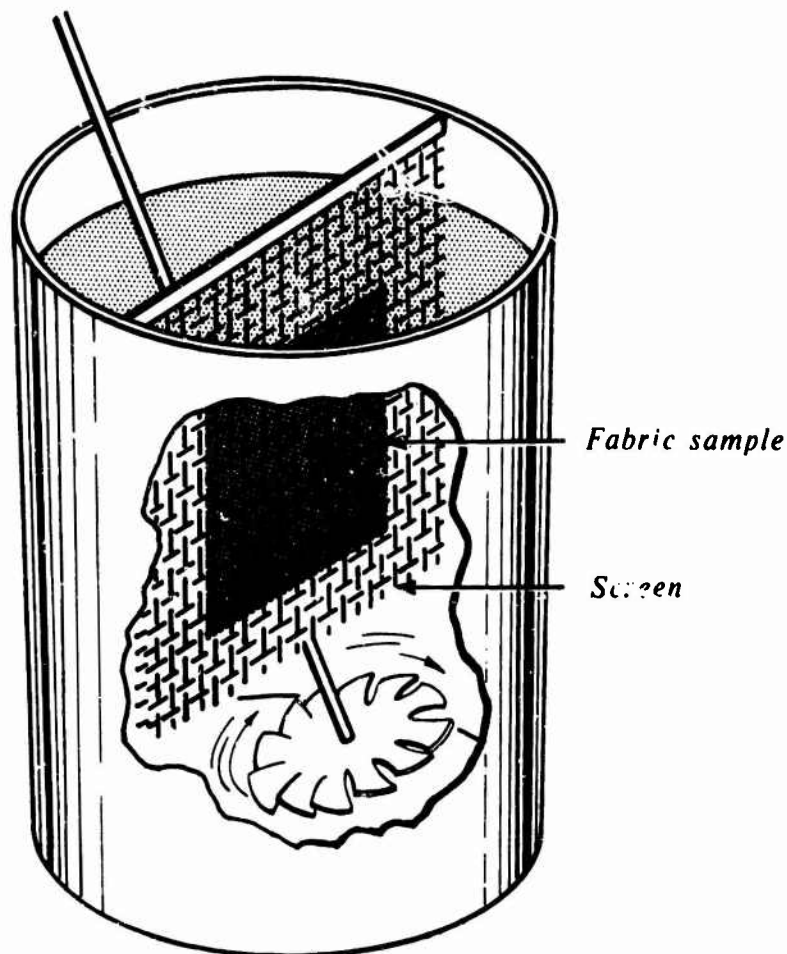
Fabric prepared from the graft copolymer in the calcium form was converted to the acid form by boiling in a dilute hydrochloric acid solution. Approximately two hundred grams of fabric were boiled with 4 liters of .01 N HCl for 30 minutes and the calcium content of the fabric was then determined. This procedure was repeated, until the calcium content was below 0.02%. The fabric was then rinsed by boiling in 4 liters of demineralized water for one half hour at least three times.

The fabric was then stored at 40% relative humidity and 23°C for at least 24 hours before use. Moisture regain under these conditions was found to be 2%.

C O P Y

APPENDIX B

Experimental Details - Calcium Uptake



Procedure A:

Samples of fabric (approx. 0.3 g each) were sandwiched between two pieces of coarse (8-mesh) stainless steel screen, and this holder was firmly mounted at an angle to direction of flow from a high-speed (est. 3000 rpm) propeller. The stainless-steel beaker containing this assembly was immersed in a constant-temperature bath, controlled to  $\pm 0.3^{\circ}\text{C}$ .

After treatment, samples were removed and promptly immersed in distilled water, then rinsed several times in fresh deionized water with vigorous agitation for 4-5 minutes. They were then squeezed dry between pressure rollers, and allowed to dry at  $24^{\circ}\text{C}$  and 40% r.h. for at least 12 hours before analysis.

C O P Y

APPENDIX C

Calcium Determination

Method:

Sample (approx. 0.3 g) was ashed over a Fisher-type blast burner (air-gas) for approximately 25 minutes. The ash was dissolved in a minimum amount of dilute HCl. The solution was then diluted to 150 ml with demineralized water, and brought to pH 12-12.5\* with 1.0 N KOH.

Hydroxy Naphthol Blue (Mallinckrodt) (0.2-0.3 g) was added. The solution was titrated to a clear blue color (from pink) with 0.05 M disodium ethylenedianime tetracetate (Mallinckrodt) (1 ml corresponds to 2.004 mgm of calcium ion).

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\*pHydrion paper

C O P Y

APPENDIX D

Standard Deviation of Calcium Determinations

Group of 60 samples, 100°C,  $\text{Ca}(\text{OAc})_2$  at 0.5, 1.0 and 2.0 percent

Standard Deviation for 60 readings = .087

Mean Value = 3.60

Standard Error of the Mean

$$\text{for 3 readings} = \frac{.087}{3} = \frac{.087}{1.732} = .0501$$

$$\text{for 5 readings} = \frac{.087}{5} = \frac{.087}{2.51} = .0336$$

C O P Y

APPENDIX E

Standard Laundering

Reference: 1965 Yearbook, American Association of Textile Chemists  
and Colorists, New York, 1965, p. B-86.

Method IIIA

Sample: 4 x 6 inches

Container: 3 1/2 x 8 inch stainless steel can containing  
100-1/4 inch steel balls.

Wash Solution: (50 ml)

0.2% soap

0.2% sodium metasilicate

Cycle: (This cycle is considered equivalent to five  
commercial launderings) Launderometer, 45 minutes  
at 160°F.

Unclassified

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13. ABSTRACT <p>The calcium salt of acrylic acid/nylon 6,6 graft polymer has been reported to show promise in flash-resistant fabrics. This report covers the initial phases of a systematic study of the preparation of the calcium form, and its characteristics in various aqueous solutions.</p> <p>The rate of sorption of calcium ion from solution was influenced primarily by changes in temperature, the desired value of 3.5 percent calcium being attained in 5 minutes at 100°C, 9 minutes at 70°C, and 64 minutes at 30°C. A continuous process for calcium treatment is therefore possible.</p> <p>The effect of solution concentration on rate of calcium sorption was much less significant, and increases in solution concentration above 1 percent caused no change in rate.</p> <p>The amount of calcium sorbed at equilibrium at 30°C was lower than 70° or 100°, suggesting a change in the character of the fiber at some intermediate temperature. The isotherm for calcium sorption was of the Langmuir type.</p> <p>Removal of the calcium was difficult with neutral detergents, but was readily accomplished with calcium complexing phosphates or with acid.</p>		

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Thermal Radiation			4			
Acid	5					
Dyes	1				6,7	
Dyeing			4			
Textiles			4			
Protection			4			
Sorption, Desorption	8		9			
Calcium	1		9		6,7,9	
Polyacrylic Acid	1					
Nylon	1					
Fibers	1,2					
Graft Copolymer	1					
Rate			7			
Temperature			6			
Concentration			6			
Equilibrium			7			

Unclassified

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